Dye removal by low cost adsorbents: Hazelnut shells in comparison with wood sawdust

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Abstract

Batch adsorption of Methylene Blue, up to $1000\,mg\,L^{-1}$, and Acid Blue 25, up to $500\,mg\,L^{-1}$, onto ground hazelnut shells was studied in comparison with sawdust of various species of wood, in order to explore the potential use of this material as low cost adsorbent for dye removal in dyehouse effluents. The adsorption kinetics was investigated according to Lagergren's model, but the best fit was achieved by a second order equation. The equilibrium data were processed according to Langmuir's model and higher adsorption capacity values towards both dyes were shown by hazelnut shells than wood sawdust.

Moreover, fixed bed adsorption of Methylene Blue was performed on hazelnut shell columns and the breakthrough curves were determined by varying bed depth, flow rate and influent concentration. The data were processed according to Bohart–Adams model and the column performances could be predicted by the bed depth service time (BDST) approach.

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1. Introduction

The colour removal from dyehouse effluents becomes day by day more than ever an important objective of wastewater treatment processes. This goal is pursued not only because the legislation requirements become more stringent, but also if the water quality for recycle purpose is taken into account. In fact, the dyes are not easily biodegradable and often are not fully removed in conventional biological plants. Therefore, a tertiary refining process is required for a complete decolorization in order to obtain an effluent of high quality suitable for reuse in the same dyehouse plant.

Among the advanced chemical or physical treatments, adsorption is considered more effective and less expensive than other technologies such as ozone or electrochemical oxidation, membrane separation, etc. Activated carbon is the most used adsorbent owing its high capacity, but needs a regeneration process being an expensive material. Many efforts, however, have been made to investigate the use of various low cost organic adsorbents [1,2]. They should be cheap, easily available and disposable without regeneration. These materials are derived from natural resources, plant wastes or industrial by-products as peat, wood, barley and rice husk, etc. [3–17]. Most of them are cellulose-based and can be used without any previous thermal or chemical treatment.

Adsorbents containing high levels of cellulose irreversibly adsorb basic dyes through coulombic attraction since negative surface charge is acquired by cellulose on contact with water [17]. Moreover, adsorption of cationic dyes is favoured as pH increases and this is consistent with cation exchange processes with acidic functional groups. However a decrease in pH causes competition for adsorption between cations and H^+. Hence the major mode of adsorption of basic dyes seems to be chemisorption [5,8]. Conversely a coulombic repulsion of an acid dye, negatively charged, can occur and low pH values could enhance the adsorption capacity of a cellulose-based adsorbent towards acid dyes, which are mostly adsorbed in a reversible process involving physical adsorption [2,17].

In the present study, the dye adsorption behaviour of ground hazelnut shells was compared with that of wood sawdust, a low cost adsorbent already experimented for dye removal [4,13,15,16]. The choice of hazelnut shells is justified by the

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Nomenclature

a	maximum value of the ratio (C_{out}/C_{in})
A	cross-sectional area of the dye molecule (m^2)
b	constant in Eq. (9)
c	constant in Eq. (9) (min^{-1})
C_e	dye concentration at equilibrium ($mg\,L^{-1}$)
C_{in}	influent concentration of the dye ($mg\,L^{-1}$)
C_{out}	effluent concentration of the dye ($mg\,L^{-1}$)
C_t	dye concentration at time t ($mg\,L^{-1}$)
C_0	initial dye concentration ($mg\,L^{-1}$)
d_p	mean diameter of particles (μm)
D	bed depth (cm)
F	dye fraction in the commercial product
k_1	pseudo-first order rate constant (min^{-1})
k_2	pseudo-second order rate constant ($g\,mg^{-1}\,min^{-1}$)
K	rate constant of adsorption ($L\,mg^{-1}\,min^{-1}$)
K_L	Langmuir constant ($L\,mg^{-1}$)
m	mass of adsorbent (g)
MW	molecular weight of the dye ($g\,mol^{-1}$)
N	adsorption capacity per volume of bed ($mg\,L^{-1}$)
N_{Av}	Avogadro number (6.019×10^{23} molecules mol^{-1})
q_e	equilibrium adsorption capacity ($mg\,g^{-1}$)
q_m	maximum adsorption capacity at equilibrium ($mg\,g^{-1}$)
q_t	adsorbed amount of dye at time t ($mg\,g^{-1}$)
Q	volumetric flow rate ($mL\,min^{-1}$)
r	correlation coefficient
R_L	separation factor
S_s	specific surface area ($m^2\,g^{-1}$ of sorbent)
t	time (min)
T_{50}	time required for the effluent to reach 50% breakthrough concentration (min)
v	linear flow rate through the bed ($cm\,min^{-1}$)
V	volume of treated solution (L)

large availability of this material, in some countries, as food industry waste. Its major use today is as combustible owing the considerable calorific value (gross value of about 17 MJ/kg of dried product) very close to that of wood. The intermediate use of both materials as sorbents does not prevent their end use as combustibles avoiding any regeneration or disposal treatment. The use of hazelnut shells as sorbent without thermal treatment was not until now proposed, whereas this material was considered in some works as source for activated carbon mostly utilized in removal of heavy metals [18–21].

The adsorption behaviour of spruce wood toward acid dyes was compared by Poots et al. [3–5] to that of peat which is chemically similar containing lignin, cellulose, fulvic and humic acids [22,23]. Hazelnut shells carry the same polar functions such as alcoholic, carbonylic, carboxylic and phenolic groups, which are potentially involved in bonding with sorbed pollutants. Therefore the sorbents tested in this work can be compared with peat, other lignocellulosic materials and activated carbon obtained from these.

The modes of contacting a solid adsorbent and wastewater are batch and fixed bed system. In the literature, most of studies dealing with dye adsorption on various materials are based on batch experiments to determine adsorption rate and equilibrium sorption capacity through concentration decay curves [24–27]. The other method involves feeding water continuously to a packed bed of granular adsorbent until breakthrough of the dye occurs in the effluent. Some theoretical models of fixed bed adsorption were developed for activated carbon and applied to other adsorbents [28–32].

In this work, several batch experiments were performed on hazelnut shells and sawdust of various species of wood towards aqueous solutions of Methylene Blue, basic dye, and Acid Blue 25. Subsequently, some runs were carried out in packed bed of ground hazelnut shells with solutions of Methylene Blue, to estimate the column adsorption performances.

2. Experimental

2.1. Adsorbents

Shells of Italian hazelnut, *Chorylus avellana* L. species, were ground in ball mill and the resulting crumbs were sieved to obtain two size ranges: 75–180 and 300–710 μm. Then the mean diameter (d_p) of the resulting particles was assumed as 125 and 500 μm.

Sawdust of four wood species was tested: walnut and cherry tree, oak, pitch-pine. They were sieved to obtain a particle size in the range 75–180 μm ($d_p = 125\,\mu m$).

Before the use, all the sorbents were washed thoroughly with deionized water and dried in air oven at 100 °C for 24 h. Bulk and

Table 1
Density and porosity of adsorbents at 20 °C

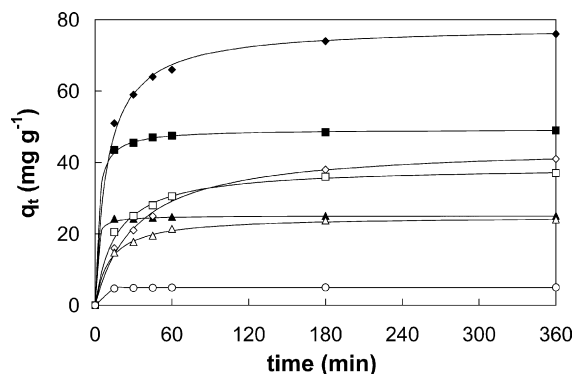| Adsorbent	Mean diameter (μm)	True density ($g\,cm^{-3}$)	Bulk density ($g\,cm^{-3}$)		Porosity	
			Dry	Wet	Dry	Wet
Hazelnut shells	125	1.395	0.606	0.459	0.566	0.671
	500	1.395	0.814	0.690	0.416	0.505
Walnut	125	1.395	0.207	0.159	0.852	0.886
Cherry	125	1.401	0.262	0.182	0.813	0.870
Oak	125	1.466	0.220	0.157	0.850	0.893
Pitch-pine	125	1.455	0.228	0.127	0.843	0.913

Fig. 1. Molecular structures of the dyes.

Fig. 2. Kinetic curves of adsorption of Methylene Blue on hazelnut shells (d_p: 125 and 500 μm) at different initial concentrations. d_p 125 μm: (♦) 1000 mg L^{-1}, (■) 500 mg L^{-1}, (▲) 250 mg L^{-1}. d_p 500 μm: (◇) 1000 mg L^{-1}, (□) 500 mg L^{-1}, (△) 250 mg L^{-1} and (○) 50 mg L^{-1}.

where C_0 is the initial dye concentration (mg L^{-1}), C_t the concentration of the solution at time t, V the volume of treated solution (L) and m is the mass of adsorbent (g).

2.4. Fixed bed experiments

The breakthrough curves were determined at 20 °C in glass columns, 10 mm i.d., containing various amounts of sorbent to achieve the prefixed bed depth. The bed was held on by a plug of glass wool and back flushed with water to eliminate air bubbles. Hence the dye solution was fed at the top by a peristaltic pump. Liquid samples were taken at prefixed intervals and analyzed.

3. Results and discussion

3.1. Kinetics in batch adsorption

The results of adsorption of Methylene Blue from aqueous solutions in the range 50–1000 mg L^{-1} by hazelnut shells of two particle sizes (d_p 125 and 500 μm) are reported in Fig. 2. The equilibrium is practically attained after 60 min with the lower size and after 180 min with the other. Moreover, the saturation values are affected by the initial dye concentration and the dye
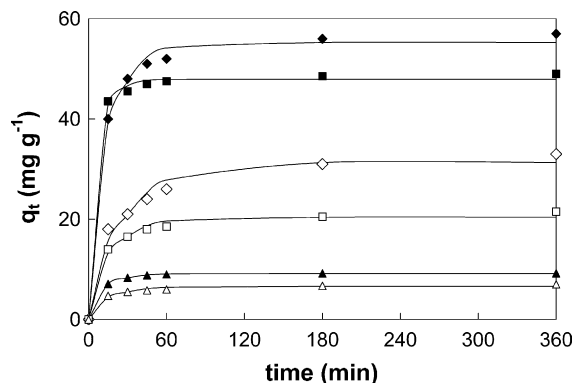
2.2. Dyes

Methylene Blue (Basic Blue 9, C.I. 52015) was Carlo Erba product, 98.5% titre. Acid Blue 25 (C.I. 62055) was the commercial product supplied by ACNA, Milano (Italy), with a titre of 31%. The molecular structures of the dyes are reported in Fig. 1.

Dye determinations were performed on a Unicam UV2 spectrophotometer at 662.5 nm for Methylene Blue and 585 nm for Acid Blue 25. Replicate measurements yielded a relative standard deviation of about 3%. The detection limit for both dyes was 0.1 mg L^{-1}.

2.3. Batch adsorption

The concentration decay curves and equilibrium sorption capacities were determined in batch experiments by shaking, at prefixed times, sealed test tubes containing 0.500 g of sorbent and 50.00 mL of dye solution. An arm shaking apparatus was preferred to a stirring device in order to minimize the fine powder formation. The shaking frequency was kept constant at 60 cycles/min. These tests were carried out in thermostatic room at 20 °C. At the end, liquid samples were taken, filtered and subjected to dye determination. The filtration was performed on small glass wool filter and the first aliquot of the filtered liquor was discarded to avoid errors due to adsorption on the filter, according to the procedure adopted by Poots et al. [3].

The kinetic data of adsorbed amount of dye at time t, q_t (in mg g^{-1} of adsorbent), were obtained by the mass balance:

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{1}$$

Fig. 3. Kinetic curves of adsorption of Acid Blue 25 on hazelnut shells (d_p: 125 and 500 μm) at different initial concentrations. d_p 125 μm: (♦) 500 mg L^{-1}, (■) 250 mg L^{-1}, (▲) 50 mg L^{-1}. d_p 500 μm: (◇) 500 mg L^{-1}, (□) 250 mg L^{-1} and (△) 50 mg L^{-1}.
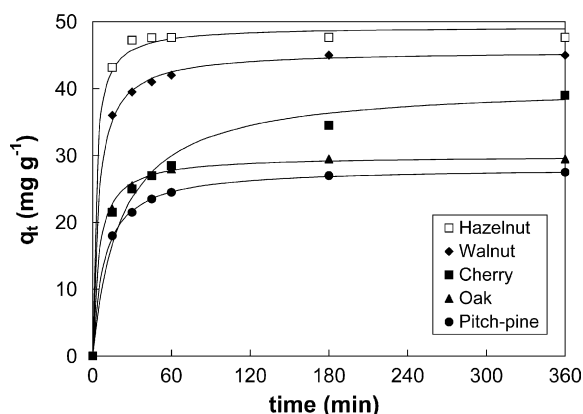
Fig. 4. Comparison between kinetic curves of adsorption of Methylene Blue ($C_0 = 500\,\mathrm{mg\,L^{-1}}$) on hazelnut shells and sawdust of various species of wood ($d_p = 125\,\mu m$).

Fig. 5. Comparison between kinetic curves of adsorption of Methylene Blue ($C_0 = 250\,\mathrm{mg\,L^{-1}}$) on hazelnut shells and sawdust of oak and pitch-pine ($d_p = 125\,\mu m$).

uptake, at the same value of C_0, is lower for the coarser particles. However at the lowest concentration ($C_0 = 50\,\mathrm{mg\,L^{-1}}$) the adsorption is very fast.

The analogous data of adsorbed amount of Acid Blue 25 in the range 50–$500\,\mathrm{mg\,L^{-1}}$ were plotted in Fig. 3 and the same trend of Methylene Blue is observed. The comparison between the adsorption behaviour of the hazelnut shells and that of wood sawdust of the same size, d_p $125\,\mu m$, is shown in Fig. 4, where the kinetic curves of adsorbed amount of Methylene Blue
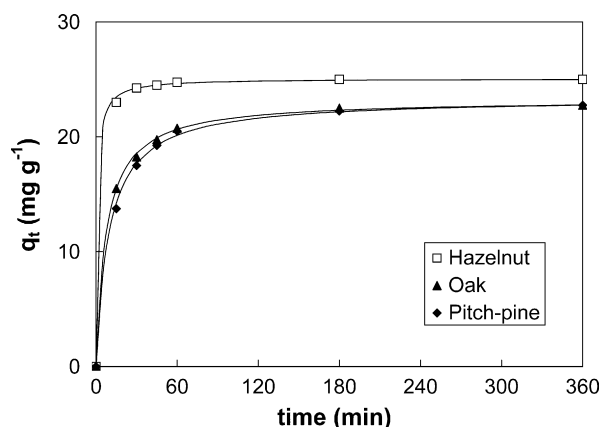
at $C_0 = 500\,\mathrm{mg\,L^{-1}}$ are plotted. The hazelnut shells show the highest uptake values followed by the walnut sawdust, whereas cherry, oak and pitch-pine achieve lower saturation levels. Moreover, while the equilibrium is practically attained after 60 min by four sorbents, the curve of the cherry sawdust is still increasing even after 120 min. At lower initial concentration, the dye uptake of the wood sawdust attains saturation values more close to the hazelnut shells, as it is shown by the data plotted in Fig. 5 for

Table 2
Kinetic parameters for various adsorbents in batch experiments at 20 °C

Adsorbent	d_p (μm)	Dye	C_0 ($\mathrm{mg\,L^{-1}}$)	q_e ($\mathrm{mg\,g^{-1}}$) experimental	First order			Second order		
					q_e ($\mathrm{mg\,g^{-1}}$) calculated	k_1 ($\mathrm{min^{-1}}$)	r^2	q_e ($\mathrm{mg\,g^{-1}}$) calculated	k_2 ($\mathrm{g\,mg^{-1}\,min^{-1}}$)	r^2
Hazelnut	125	Methylene Blue	1000	76.0	71.0	0.071	0.975	76.1	0.0013	0.9999
			500	49.0	47.7	0.157	0.997	48.9	0.0088	1
			250	25.0	24.7	0.264	0.999	25.0	0.0390	1
Hazelnut	500	Methylene Blue	1000	41.0	39.3	0.024	0.978	41.0	0.0007	0.9995
			500	37.0	35.0	0.043	0.966	37.1	0.0016	0.9997
			250	24.0	22.8	0.055	0.974	24.0	0.0036	0.9998
			50	5.0	4.9	0.198	0.999	5.0	0.2164	1
Hazelnut	125	Acid Blue 25	500	57.0	55.3	0.065	0.995	58.1	0.0026	1
			250	49.0	47.9	0.119	0.998	49.3	0.0088	1
			50	9.2	9.2	0.078	0.999	9.3	0.0349	0.9999
Hazelnut	500	Acid Blue 25	500	33.0	31.3	0.037	0.982	34.6	0.0016	0.9996
			250	21.5	20.4	0.055	0.989	22.0	0.0044	0.9998
			50	7.0	6.6	0.059	0.985	7.2	0.0138	0.9998
Walnut	125	Methylene Blue	750	57.8	54.2	0.046	0.982	59.5	0.0012	0.9995
			500	45.0	43.6	0.085	0.993	45.7	0.0050	0.9999
			50	5.0	5.0	0.224	0.999	5.0	0.3835	1
Cherry	125	Methylene Blue	750	39.8	37.1	0.043	0.976	41.2	0.0015	0.9992
			500	39.0	35.5	0.038	0.957	40.7	0.0011	0.9973
			50	5.0	5.0	0.247	0.999	5.0	0.1555	1
Oak	125	Methylene Blue	500	29.5	29.0	0.072	0.997	29.9	0.0071	0.9999
			250	22.8	22.1	0.059	0.994	23.3	0.0057	1
			50	5.0	5.0	0.224	0.999	5.0	0.3830	1
Pitch-pine	125	Methylene Blue	500	27.5	26.6	0.055	0.994	28.2	0.0040	1
			250	22.8	22.2	0.049	0.997	23.4	0.0044	1
			50	5.0	5.0	0.224	0.999	5.0	0.3830	1

$C_0 = 250$ mg L^{-1}. At still lower concentration ($C_0 = 50$ mg L^{-1}) the wood sawdust of all types shows very fast adsorption, like hazelnut shells.

At first the kinetics of adsorption was investigated according to a first order equation derived from the widely used Lagergren equation [11,15,25–27]:

$$q_t = q_e(1 - e^{-k_1 t}) \tag{2}$$

where q_e is the equilibrium adsorption capacity (mg g^{-1}), while k_1 is the pseudo-first order rate constant (min^{-1}). The q_e and k_1 values were calculated by SigmaPlot, by SPSS Inc., computer program and the fitting could be enough satisfactory, as it is shown by the regression parameters reported in Table 2. Nevertheless, the fitting is less acceptable at long times and there is some disagreement between experimental and calculated q_e values.

Therefore, the data were further processed according to a second order kinetic model on the basis of the following differential equation:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{3}$$

where k_2 is the rate constant of pseudo-second order adsorption (g mg^{-1} min^{-1}). The integration of Eq. (3) for the boundary condition $q_t = 0$ at $t = 0$ gives:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \tag{4}$$

which can be linearized as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{5}$$

Table 3
Langmuir parameters of adsorption isotherms at 20 °C

Adsorbent	Dye	d_p (µm)	q_m (mg g^{-1})	K_L (L mg^{-1})	r^2	C_0 (mg L^{-1})	R_L	S_s (m^2 g^{-1})
Hazelnut	Methylene Blue	125	76.9	0.36	0.999	1000	0.003	
						500	0.006	
						250	0.011	
		500	41.3	0.15	0.999	1000	0.007	
						500	0.013	
						250	0.026	
	Acid Blue 25	125	60.2	0.043	0.993	500	0.044	21.6
						250	0.085	
						50	0.317	
		500	40.8	0.054	0.966	500	0.036	14.6
						250	0.069	
						50	0.270	
Walnut	Methylene Blue	125	59.17	0.15	0.992	750	0.009	
						500	0.013	
						50	0.118	
	Acid Blue 25	125	36.98	0.025	0.997	500	0.074	13.3
						250	0.138	
						50	0.444	
Cherry	Methylene Blue	125	39.84	1.08	0.999	750	0.001	
						500	0.002	
						50	0.018	
	Acid Blue 25	125	31.98	0.018	0.998	500	0.100	11.5
						250	0.182	
						50	0.526	
Oak	Methylene Blue	125	29.94	0.30	0.999	500	0.007	
						250	0.013	
						50	0.063	
	Acid Blue 25	125	27.85	0.016	0.999	500	0.111	10.0
						250	0.200	
						50	0.556	
Pitch-pine	Methylene Blue	125	27.78	0.43	0.999	500	0.005	
						250	0.009	
						50	0.044	
	Acid Blue 25	125	26.19	0.033	0.997	500	0.057	9.4
						250	0.108	
						50	0.377	

The linear plots of t/q_t versus t show an excellent agreement with the experimental data for all the sorbents. The regression parameters for the second order kinetic model are also reported in Table 2. The squared correlation coefficients (r^2) are mostly higher than 0.999 and the calculated q_e values are in good agreement with the experimental results. Moreover, the interpolating curves plotted in Figs. 2–5 were drawn on the basis of this model.

In conclusion, the adsorption kinetics of ionic dyes on hazelnut shells can be better explained by a second order model and this pattern is shown also in the adsorption of Methylene Blue onto wood sawdust of various species. A similar trend was already observed by some authors in dye adsorption on various materials [25–27].

3.2. Adsorption isotherms

The equilibrium data were processed according to the well known Freundlich and Langmuir isotherms. The fitting of Langmuir's model was found more satisfactory, hence only these results are reported in Table 3. The Langmuir isotherm was expressed as:

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \tag{6}$$

where q_e is the equilibrium adsorption capacity (mg g^{-1}), q_m the maximum amount of dye adsorbed (mg g^{-1}) corresponding to monolayer coverage, K_L the Langmuir constant (L mg^{-1}) and C_e is the equilibrium concentration of dye in the bulk solution (mg L^{-1}). The values of K_L and q_m were calculated from the linearized form of Eq. (6) by plotting C_e/q_e versus C_e.

From Langmuir's isotherm the dimensionless separation factor R_L is derived as follows:

$$R_L = \frac{1}{1 + K_L C_0} \tag{7}$$

R_L values in the range from 0 to 1 indicate favourable adsorption [5,15,26–27,32]. In Table 3 the calculated R_L values are also reported and are mostly lower than 0.1, confirming very favourable conditions in adsorption process with all the experimented materials toward both dyes in a wide range of initial concentrations. Hazelnut shells, however, show higher values of the maximum adsorption capacity, q_m, than wood sawdust.

The q_m values obtained in sorption of Acid Blue 25 enabled to estimate the specific surface area S_s according to the equation applied by Poots et al. [3,4] to peat and wood for adsorption of the same dye:

$$S_s = \frac{F q_m N_{Av} A}{MW \times 1000} \tag{8}$$

where S_s is the specific surface area (m^2 g^{-1} of sorbent), F the dye fraction in the commercial product (0.31), N_{Av} the Avogadro number (6.019×10^{23} molecules mol^{-1}), A the cross-sectional area of the dye molecule (m^2) and MW is the molecular weight of the dye (416 g mol^{-1}). The cross-sectional area of Acid Blue 25 was taken as 80 Å^2.

The estimated values of S_s are listed also in Table 3 and indicate surface areas of oak and pitch-pine very close to that reported for peat of size range 150–250 µm (9.0 m^2 g^{-1}) and 50% higher than the value reported for spruce wood (6.4 m^2 g^{-1}) [4]. In any case hazelnut shells and the other sawdusts show higher surface areas. Moreover the lower adsorption capacity of the coarser particles of hazelnut shells can be justified by the lower surface area as in the case of peat [3]. The same calculations using Methylene Blue isotherm yielded much higher values of surface area, which were justified by a multilayer adsorption due to chemisorption process involving ion exchange reactions [5].

The q_m value found in sorption of Methylene Blue on hazelnut shells with d_p 500 µm (41.3 mg g^{-1}) is about five times higher than that reported for activated carbon obtained from the same material (8.82 mg g^{-1}) although a strong increases of surface area (793 m^2 g^{-1}) due to thermal treatment [20]. This confirms that thermal activation develops high microporous structure, which are inaccessible to dye molecules and conversely destroys functional groups on the surface, which are involved in the adsorption mechanism. However the adsorption capacity toward Methylene Blue of hazelnut shells with d_p 125 µm (76.9 mg g^{-1}) can be compared with that of powdered activated carbon obtained from coconut shells (48 mg g^{-1}) and babassu (79 mg g^{-1}) [33]. Coir pith, another agricultural biomass, shows even higher adsorption capacity (120 mg g^{-1}) but this result is strongly reduced by carbonization [8]. Moreover, the wood sawdust shows much higher adsorption capacity (28–59 mg g^{-1}) than that reported for beech sawdust (9.78 mg g^{-1}) [15].

3.3. pH range

The influence of the pH on the adsorption behaviour of dyes onto various adsorbent was considered by many authors [8,11,15,16]. In the case of cellulose materials it was reported that the anionic dyes show a sorption increase below pH 4, while cationic dyes showed maximum adsorption at pH 3–4 [11]. Since the introduction of strong acid or bases could alter the surface properties of the sorbents as well as the ionic character and aggregation state of the dyes, in our experiences the pH values were not adjusted. In fact the system was already acidic (pH 2.3–3.8) owing the presence of carboxylic and phenolic groups and when equilibrium was reached the increase was limited to 0.3–0.5 units. Therefore the runs were carried out in the range of pH 2.5–4.2, quite favourable for comparison between the adsorbents toward anionic as well as cationic dye.

3.4. Column studies

Fixed bed experiments were carried out on Methylene Blue solutions at influent concentrations of 100 and 500 mg L^{-1} with hazelnut shells of lower size (d_p 125 µm). The breakthrough curves of the ratio between effluent and influent concentration (C_{out}/C_{in}) versus time for various bed depth at flow rate of 18 mL min^{-1} and $C_{in} = 100$ mg L^{-1} are shown in Fig. 6. The breakthrough times for bed depth of 8.3, 13 and 19.3 cm are 75, 110 and 155 min, respectively, showing a linear increase with the bed depth. The shape and slope of the curves are slightly dif-
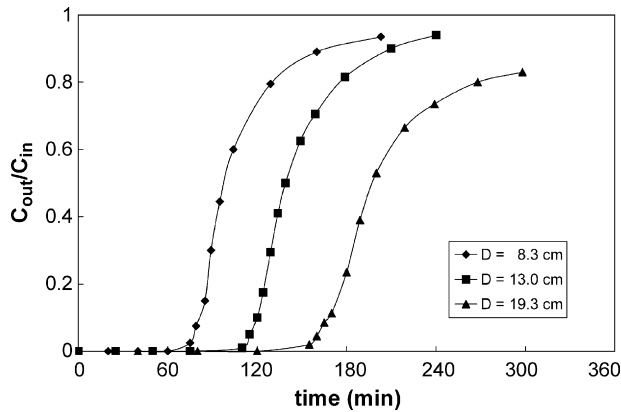
Fig. 6. Effect of bed depth on breakthrough curves in fixed bed adsorption of Methylene Blue on hazelnut shells ($d_p = 125\,\mu m$). Conditions: $C_{in} = 100\,mg\,L^{-1}$, $Q = 18\,mL\,min^{-1}$.
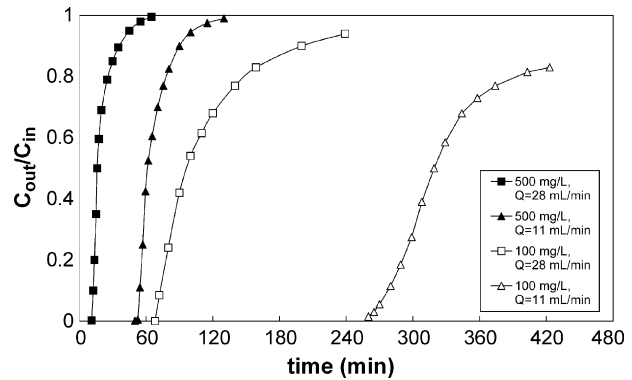

Fig. 7. Effect of influent concentration at two flow rates on breakthrough curves in fixed bed adsorption of Methylene Blue on hazelnut shells ($d_p = 125\,\mu m$). $D = 19.5\,cm$.

ferent with the variable bed depths, but the curve of the longer bed (19.3 cm) tends to be more gradual, meaning the column is difficult to be completely exhausted, as in the case of adsorption of reactive dye onto metal hydroxide sludge [31]. The results of other runs at constant bed depth with various flow rates similarly indicates that when increasing the flow rate, breakthrough time linearly decreases. This is due to decreased contact time between the dye and the sorbent at higher flow rates. Similar effects of bed depth and flow rate on breakthrough curves obtained in dye adsorption on packed-bed of other adsorbents were observed by many authors [28–32].

The effect of the influent concentration (100 and 500 mg L^{-1}) on the breakthrough curves at a constant bed depth (19.5 cm) at two flow rates (11 and 28 mL min^{-1}) is compared in Fig. 7. Increasing the initial concentration strongly decreases the breakthrough time and the curves become very steep. An increase of inlet dye concentration increases the slope of the breakthrough curve, reducing the volume treated, as in the case of adsorption of dyes onto granular activated carbon and zeolite [29].

Moreover, the data were processed according to Bohart–Adams model [34]. The equation of the sigmoidal curve was considered as:

$$\frac{C_{out}}{C_{in}} = \frac{a}{1 + e^{b-ct}} \tag{9}$$

in which a is the maximum value of the ratio C_{out}/C_{in}, while b and c are related to the midpoint time: $C_{out} = 0.5aC_{in}$ for $t = b/c$. The factor a was introduced instead of unity taking into account that the curves are not perfectly symmetrical for $C_{out} = 0.5C_{in}$.

The results of calculation of a, b and c by SigmaPlot software are collected in Table 4 and the squared correlation coefficients (r^2) are very satisfactory.

Eq. (9) can be rearranged as:

$$\ln\left(\frac{aC_{in}}{C_{out}} - 1\right) = b - ct \tag{10}$$

which is equivalent to the linearized Bohart–Adams equation, modified by introducing the factor a:

$$\ln\left(\frac{aC_{in}}{C_{out}} - 1\right) = \frac{KND}{v} - KaC_{in}t \tag{11}$$

Table 4
Calculated parameters of Methylene Blue adsorption onto columns of hazelnut shells ($d_p = 125\,\mu m$)

| D (cm)	C_{in} (mg L^{-1})	Q (mL min^{-1})	v (cm min^{-1})	a	b	c (min^{-1})	r^2	K ($\times 10^3$ L mg^{-1} min^{-1})	N ($\times 10^3$ mg L^{-1})
8.3	100	28	35.7	0.896	6.18	0.112	0.976	1.3	21.3
	100	18	22.9	0.878	11.49	0.119	0.985	1.4	23.3
	100	11	14.0	0.890	10.26	0.068	0.985	0.8	22.6
	100	6	7.6	0.666	30.81	0.091	0.988	1.4	20.8
13.0	100	28	35.7	0.899	7.77	0.112	0.974	1.2	17.1
	100	18	22.9	0.878	12.80	0.093	0.982	1.1	21.4
	100	11	14.0	0.835	14.96	0.068	0.992	0.8	19.8
	500	11	14.0	0.933	5.76	0.151	0.974	0.3	19.2
	500	6	7.6	0.821	7.27	0.098	0.986	0.2	17.8
19.5	100	28	35.7	0.869	6.54	0.068	0.970	0.8	15.2
	100	18	22.9	0.788	14.83	0.078	0.993	1.0	17.7
	100	11	14.0	0.804	17.69	0.057	0.997	0.7	18.0
	500	28	35.7	0.910	7.15	0.440	0.968	1.0	13.5
	500	11	14.0	0.913	12.48	0.201	0.964	0.4	20.4
	500	6	7.6	0.815	10.70	0.094	0.994	0.2	18.2
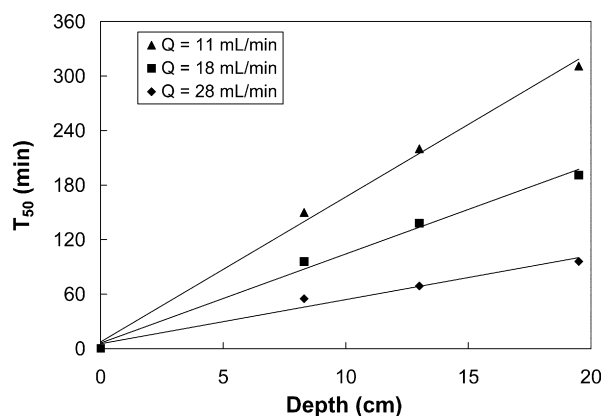
Fig. 8. BDST plot for various flow rates in fixed bed adsorption of Methylene Blue on hazelnut shells ($d_p = 125\,\mu m$). $C_{in} = 100\,mg\,L^{-1}$.

where K is the rate constant of adsorption ($L\,mg^{-1}\,min^{-1}$), N the adsorption capacity per volume of bed ($mg\,L^{-1}$), D the bed depth (cm) and v is the linear flow rate through the bed ($cm\,min^{-1}$).

By comparison between Eqs. (10) and (11), if it is assumed that $b = KND/v$ and $c = KaC_{in}$ (min^{-1}), the rate constant K can be calculated from a and c, while the adsorption capacity N from K and b.

The adsorption capacity per volume of bed has an average value of $19.1\,mg\,mL^{-1}$ and the amount of dye adsorbed per unit mass of adsorbent is in the range $50–59\,mg\,g^{-1}$, about one fourth lower than the equilibrium value found in batch adsorption ($76.9\,mg\,g^{-1}$). At the same bed depth and flow rate, the rate constant K tends to decrease as the influent concentration increases. Eq. (11) can be rearranged as:

$$t = \frac{ND}{aC_{in}v} - \frac{1}{KaC_{in}}\ln\left(\frac{aC_{in}}{C_{out}} - 1\right) \qquad (12)$$

which is the modified bed depth service time (BDST) equation [35], yielding a straight line when the time corresponding to a required ratio (service time) is plotted versus the bed depth. Moreover at 50% breakthrough ($C_{out} = 0.5aC_{in}$ and $t = T_{50}$) the logarithmic term reduces to zero and the curve of T_{50} versus D should be a straight line passing through the origin if the adsorption data follow the BDST model. The graph of Fig. 8 shows that the results of the fixed bed experiments are well interpolated by straight lines passing very close to the origin, hence the bed performances could be predicted by the equation of BDST model.

4. Conclusion

The results obtained in batch adsorption of Methylene Blue and Acid Blue 25 onto hazelnut shells in comparison with wood sawdust showed that the adsorption kinetics with both adsorbents can be explained by a second order equation better than Lagergren's first order model. The equilibrium data agree with Langmuir isotherms and the adsorption capacity values in the same experimental conditions are higher for hazelnut shells, hence this material could be used more advantageously than wood sawdust as low cost adsorbent in colour removal from dyehouse effluents. Moreover the adsorption capacity values of hazelnut shells toward Methylene Blue are even higher than those reported for activated carbon obtained from the same material and some other lignocellulosic sources.

The trend of breakthrough curves obtained in fixed bed adsorption of Methylene Blue on hazelnut shell columns was found similar to that observed with other adsorbents. The data were processed according to Bohart–Adams model and the column performances could be predicted by the bed depth service time (BDST) approach.

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